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The analytical utility of negative-ion detection is evaluated for the determination of nonmetals by inductively coupled plasma-mass spectrometry. The background spectrum is simpler than for positive ions although the baseline background level is a factor of 50 times higher. The only elemental species that can be detected with reasonable sensitivity as negative ions are the halogens. For these ions, calibration curves are linear over at least four orders of magnitude and detection limits range from 10 to 400 ng/mL. Other characteristics that are evaluated include isotope ratios, matrix effects caused by the associated cation or the anion speciation, and polyatomic-ion formation.

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THE DETECTION OF NEGATIVE IONS BY

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

by

George H. Vickers, Daniel A. Wilson, and Gary M. Hieftje

Accepted for Publication

in

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INTRODUCTION

Inductively coupled plasma-mass spectrometry (ICP-MS) can determine almost every element in the periodic table with extremely high sensitivity. For metals, in particular, detection limits are frequently in the sub-ng/mL range (1). These species have ionization energies that are well below that of Ar (15.76 eV), and therefore exist in the ICP mostly as positive ions and at levels approaching 100%.

In contrast, many nonmetals (eg. F) have ionization energies close to or greater than that of Ar and will not form positive ions to the same extent. Consequently, the detection sensitivity for many of these elements is substantially lower. Conveniently, nonmetals typically have higher electron affinities than do metals, so they are likely to form negatively charged species in the ICP or in the extraction process that leads to the mass spectrometer. To extend the analytical utility of ICP-MS to include these elements, the use of negative-ion detection as an alternate approach has been evaluated in the present study.

Previous attempts in ICP-optical emission spectroscopy (OES) to determine nonmetals have yielded only limited practical utility (2-11). Although emission from many of these elements can be observed, it is typically detected only when relatively high concentrations of the analyte are present in the sample. As a result the halogens, for example, have detection limits by ICP-OES in the low μg/mL to high ng/mL range (10-11).

Recently, dramatic improvements have been made towards increasing the sensitivity for nonmetals by detecting vacuum-ultraviolet radiation from the ICP through an optical sampling orifice (12). The design of the optical sampling orifice is based on the interface design of an

ICP-MS instrument, and enables the integration of the emission signal through the axial channel in the center of the ICP. By using this arrangement, detection limits for the halogens are in the low ng/mL range.

Several workers have investigated the determination of nonmetals as positive ions by plasma source-MS. In the first such report (13), an ICP-MS instrument was used as an elemental detector for organic species separated by gas chromatography. Detection limits varied greatly, from high ng/s to low pg/s; these variations were reported to be caused by differences in the ionization energies of the nonmetals. Another paper (14) evaluated a microwave-induced plasma (MIP) as the ion source for a quadrupole mass spectrometer into which halogenated organic compounds were introduced as gaseous samples. Because the first ionization energy (I.P.) of Ar is comparable to those of the halogens, He (I.P. = 24.48 eV) was used as the plasma-support gas to enhance sensitivity. Detection limits were found to be in the low pg/s range. Finally, an ICP supported with He has been studied for use in ICP-MS to measure nonmetals in gaseous organic compounds (15). An estimated detection limit for Br was 0.2 pg/s. While the second two reports demonstrate substantial improvements over the first, plasmas that are supported with He frequently become unstable and lose sensitivity upon the introduction of water. This characteristic would greatly reduce their utility for the determination of nonmetals in aqueous solutions.

The first published report of detecting negative ions by plasma source-MS was by Douglas and French (16). Although the authors used a MIP instead of an ICP as their ion source, the feasibility of negative-ion detection was demonstrated. Their paper illustrated a spectrum of

bromine ions (Br⁻) from a 10 ppm solution of NaBr. While the results were only preliminary, they suggested the posibility of detecting halogens as negative ions in the parts-per-billion range. Since that time, several researchers have proposed negative-ion detection as a potential research area (1,17).

In the present report, results obtained for the detection of negative ions with an inductively coupled plasma-mass spectrometer are presented and compared with those for positive-ion detection. Additionally, analytical characteristics that were evaluated in the negative-ion mode include the mass-spectral background, linear dynamic range, detection limits, isotope ratios, matrix effects caused by the associated cation or anion speciation, and polyatomic-ion formation.

EXPERIMENTAL SECTION

Instrumental. The ICP-MS instrument used for this study is described in detail elsewhere (18), and consists of a commercial ICP power generator and impedance-matching network (Plasma-Therm Model HFP 2500F, Kresson, NJ) coupled to a quadrupole mass spectrometer system (Balzers Model QMG 511, Hudson, NH) using a two-stage, differentially-pumped interface and a three-stage vacuum system.

Operating conditions for the ICP in the positive and negative-ion modes are the same except for minor changes in the nebulizer-gas flow rate; these parameters are listed in Table I. The low gas flow rates are typical for the MAK torch (Sherritt Gordon Mines, Fort Saskatchewan, Alberta, Canada) employed in this study.

The mass spectrometer has two different detection modes when operated for positive ions, current monitoring and ion counting;

however, because it is necessary to electrically float the secondary-electron multiplier detector in order to measure negative ions with our instrument, we are limited to use of the ion-counting system. Otherwise, operation of the mass spectrometer in the negative-ion mode is accomplished simply by switching the polarity of the ion-optic potentials, excluding the instrument bias potential, and making minor adjustments to values for the instrument bias and second-stage ion optic potentials.

The function of the instrument bias potential is to offset the plasma potential and to be a kinetic-energy selection parameter (19). Therefore, in the positive-ion mode it will equal the sum of the plasma potential and the kinetic energy gained by ions in the supersonic expansion; in the negative ion mode it equals the difference between these quantities. Because the magnitude of the plasma potential (approximately +15 V) is greater than the kinetic energy from the expansion (0 - 8.5 eV), the instrument bias potential is always positive, even in the negative-ion detection mode.

Sample introduction employs a glass-concentric pneumatic nebulizer and a Scott-type, double-pass spray chamber, both constructed locally. To maintain a constant and controllable sample-introduction rate, a peristaltic pump (Gilson Minipuls 2, Middleton. WI) is used. Because early experiments revealed that halogens exhibit significant memory effects, flow injection was used for the investigation of matrix cation and anion effects. Our flow-injection system has been descibed previously (20) and involves a four-way injection valve with an 85-μL sample loop inserted into the sample-introduction line. This system was found earlier to have a precision for 10 replicate measurements made

within 30 minutes of approximately 10% and to sufffer a factor of three

loss in sensitivity compared to continuous sample introduction.

However, during the present investigation, the precision was typically

closer to 5% for a similar experiment. In addition, signals were

obtained with a similar intensity to those encountered in continuous

sample introduction (cf. Table I), but by increasing the sample uptake

rate to 1.00 mL/min and optimizing the nebulizer gas flow.

Reagents. Stock solutions of As, B, Br, Cl, F, I, P, S, Se, Si and

Te were made at a concentration of 1000 μg/mL using analytical reagent-

grade chemicals in distilled-deionized water. In situations where it

was necessary to use an acid to dissolve the sample (As, Se, Te), nitric

acid was used exclusively. From these stock solutions, standards of the

appropriate concentrations were prepared daily.

To study the effect of the associated cation and the anionic form

of the analyte, analytical reagent-grade samples of NaCl, KCl,

$SrCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 2H_2O$, $CuCl_2$, KBr, $KBrO_3$, NaI, $NaIO_3$,

$Ba(ClO_3)_2 \cdot H_2O$ and $NaClO_4$ were dried for several days at 110 °C. From

these samples, 1000 μg/mL (as the halogen) stock solutions were prepared

and used to make 10 μg/mL standards.

To investigate the extent of polyatomic-ion formation, stock

solutions of 1000 μg/mL NO_3^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} were prepared from

the Na salts. The stock solutions were diluted to prepare a standard

solution containing 10 μg/mL of each anion. In addition, two other

standard solutions were made with a concentration of 10 μg/mL in the

halogens using the Cl^-, Br^-, I^- and the ClO_3^-, BrO_3^-, IO_3^- stocks.

Procedures. <u>Background Scans.</u> Scans covering the spectral region

from m/z — 0 to 100 were collected in both the positive and negative-ion

modes at a rate of 10 s/(m/z) with a 0.3-s time-constant filter and using distilled-deionized water as the blank (18). Prior to each scan, the operating conditions were optimized for chlorine using the residual Cl$^-$ (m/z - 35) in the blank. For all scans the quadrupole mass spectrometer was adjusted to provide baseline resolution between adjacent peaks of equal, full scale intensity.

Signal-to-Noise Comparison. The S/N ratios for the 11 nonmetals were determined in both the positive and negative-ion modes at a concentration of 10 μg/mL. The system was optimized individually for maximum sensitivity of each analyte; the optimal conditions were found to be essentially the same for both detection modes and all analytes. The signal was then averaged for 100 s with a 1-s time constant. After the sample was allowed to wash out for several minutes, the background level and noise were recorded at the same mass setting. Several replicate measurements were performed for each of the analytes. For the comparison, S/N was defined as the background-corrected signal divided by one-fifth of the background peak-to-peak noise (21).

Calibration Curves and Detection Limits. Calibration curves were produced from background-subtracted signals for each of the halogens by means of a decade-dilution scheme. A linear-regression fit to the curve of S/N versus analyte concentration for the values from within approximately two orders of magnitude of the detection limit was used to determine the detection limit as the concentration at S/N - 3.

Isotope Ratios. Isotope ratios were determined for chlorine and bromine from three successive scans over the mass region of interest. Analyte concentrations were 10 μg/mL and the scan rate was 10 s/(m/z) with baseline resolution between adjacent peaks. A background scan with

distilled-deionized water as a blank was then subtracted from each analyte scan to determine the signal magnitudes.

Matrix Cation and Anion Effects. Flow injection was used to introduce chloride salts of Ba, Co, Cu, K, Na and Sr. Six injections of 10 μg/mL Cl were made for each cation in a random order to eliminate the possibility of systematic errors and those associated with instrument drift.

To investigate the anion-speciation effect, the halide ion signal was compared for ClO_3^-/Cl^-, ClO_4^-/Cl^-, BrO_3^-/Br^- and IO_3^-/I^-. Six injections of these 8 solutions, each containing 10 μg/mL of the halogen were made in random order. For each comparison, the identity and concentration of the associated cation remained constant.

Polyatomic Ion Formation. The three 10 μg/mL mixtures described above were analyzed for polyatomic ion formation using identical parameters to those employed in the background scans, only in the negative-ion detection mode. By subtracting the background scan, differences in the spectra could be identified and appropriate assignments made.

RESULTS AND DISCUSSION

Background Scans. The negative-ion background spectrum of distilled-deionized water is displayed in Figure 1. In comparison to the background spectrum for positive ions obtained with the same instrument (18), the negative-ion scan has considerably fewer background peaks; accordingly, problems associated with background spectral interferences should be less significant. However, the baseline background level is a factor of approximately 50 higher (1000 cps), and

the corresponding increase in the background noise level should yield

poorer detection limits. The higher baseline background and noise level

is most likely caused by electrons which reach the secondary electron

multiplier. The sources of these electrons are probably the ICP,

collisions among high-energy ions and/or photon-induced ionization.

The most abundant species in the negative-ion background spectrum

are O^- and OH^- at m/z = 16 and 17, respectively. Additional peaks that

have been identified include H_2O^- (m/z = 18), either F^- contamination or

H_3O^- (m/z = 19), and O_2^- (m/z = 32); the assignment of several other

peaks is still uncertain. For example, there are three groups of peaks

in the background spectrum at approximately m/z = 40, 20 and 13, in

decreasing order of magnitude. Spectral features such as these have

been observed also by others who have begun to explore negative ion

detection (22) and are believed to be caused by extremely high-energy,

positively charged argon species (Ar^+, Ar^{2+} and Ar^{3+}). These argon

species are probably scattered through the ion optics, transmitted

through the quadrupole at the appropriate mass setting, followed by

collision with the internal surfaces of the instrument. These

collisions result in the release of secondary electrons which are

accelerated toward and detected by the secondary electron multiplier.

Because of their high energies, the species in these groups of peaks

cannot be adequately resolved into the isotopic constituents of argon.

In support of this hypothesis, the penetration of positively charged

ions through ion optics which are biased with a positive potential has

previously been reported (23).

Signal-to-Noise Comparison. Values of the S/N for the 11 nonmetals

studied in this paper are listed in Table II for both the positive and

negative-ion detection modes. For F, Si (positive ion mode only), S, Cl and Se, there are background peaks upon which the analyte signal must be detected, a situation that reduces the S/N. In addition, intense background peaks coincide with the most abundant isotopes of S and Se (m/z = 32 and 80, respectively) in both positive and negative-ion detection modes, so these isotopes are not optimal for analysis. The second most abundant isotope has been selected in each case.

The only element that is not detected as a positive ion is F; this is not surprising for several reasons. First, F is monoisotopic at m/z = 19. At this mass in the positive-ion spectrum, there is a strong background peak for H_3O^+ at about 30,000 cps. Second, the first ionization potential for F is 17.42 eV, 1.66 eV higher than that for Ar. Therefore, F is not likely to exist to a great extent in the ICP as a positive ion.

From Table II, only the halogens can be detected in our instrument as negative monatomic ions generated from aqueous sample solutions. Both F and Cl produce significantly higher S/N as negative ions than as positive ions, even though their detection is severely background-limited. In contrast, Br has approximately the same detectability as a positive or negative ion, and I is nearly an order of magnitude worse as a negative ion.

An obvious similarity among the halogens is their ability to attract electrons; i.e., their electron affinity. These elements possess the four highest values for electron affinity in the periodic table and might be expected to exhibit a correlation between this value and the analytical signal; Figure 2 shows this relationship. In Figure 2, signals have been corrected for isotopic abundance and for

instrumental mass bias (20) to values corresponding to m/z - 35. This mass-bias correction was actually determined for positive ions; however, because there were no significant adjustments made to the ion optics or the quadrupole system except to switch their polarity, this correction should be valid also for negative ions. The regression line for this plot can be extrapolated to the electron affinity for S (2.07 eV), and would show the signal from 10 μg/mL to be lost in the background. Because S has the fifth highest electron affinity, it is not surprising that no elements other than the halogens were detected here as negative ions. Of course, this observation will be instrument-dependent; preliminary results of others (22) have shown that additional elements can be detected as negative ions.

Calibration Curves and Detection Limits. Analytical calibration curves were determined for each of the halogens. The slopes for plots of log(Signal) versus log(Concentration) determined by linear regression range from 0.958 (Br) to 1.04 (F) and have r^2-values of either 0.999 or 1.00. In all cases the linear dynamic range extends over at least four orders of magnitude from the detection limit to an upper concentration of 1000 μg/mL. Above 1000 μg/mL, the glass-concentric, pneumatic nebulizer becomes unstable; also, the signals at 1000 μg/mL are approaching a counting rate above which the working curves will bend downward because of counting statistics (18).

Detection limits for the halogens are listed in Table III. The values for F and Cl are higher than expected because they fall on significant background peaks. The interferences are most likely low levels of these elements in the blank. In a non-blank-limited situation, the detection limits for F and Cl would be approximately 30

and 20 ng/mL, respectively. Instrumental mass bias restricts the detection limits from being ordered according to the electron affinities.

These values represent some of the best ICP-MS detection limits reported for the halogens in aqueous solution. Moreover, the instrument used in this negative-ion study has been shown not to be as sensitive as others; our detection limits for positive ions are currently 1-2 orders of magnitude higher (18) than those of others. Even lower detection limits for the halogens might therefore be achieved using ICP-MS.

Isotope Ratios. Isotope ratios were measured for $^{35}Cl/^{37}Cl$ = 3.054 and $^{79}Br/^{81}Br$ = 1.023, the only two isotopes for each of these elements. Both F and I are monoisotopic, so they have no isotope ratio. For both ratios measured, the agreement between the experimental and literature values ($^{35}Cl/^{37}Cl$ = 3.087, $^{79}Br/^{81}Br$ = 1.022) is excellent. The relative standard deviations of the measured values are 4.1% (Cl) and 2.5% (Br), which are very good considering that the results are derived from three background-subtracted scans taken at 10 s/(m/z). The Cl precision is slightly poorer than that for Br, probably because the measured ratio is further from unity and because the Cl peaks lie on top of a background spectral interference.

Matrix Cation and Anion Effects. The influence of a variety of cations on a Cl⁻ signal is shown in Figure 3. The potentially interfering cations cover a fairly wide mass range, have little similarity in their first ionization potentials, and four are doubly charged in solution, making their molar concentration half that of the other two (the Cl⁻ concentration is the same in all cases). Regardless, there is no significant influence of the matrix cation.

The observed linearity of the calibration curves is further support for the lack of a cation matrix effect in the form of ionization enhancement. The reagents used for these solutions were alkali salts (Na and K) whose cations have very low first ionization potentials. If a cation enhancement effect existed, it would occur at high concentrations and would cause the calibration curves to bend upward.

Another kind of matrix effect could be caused by the anion species which contains the analyte. However, Table IV suggests that no such interference occurs. For all anion pairs except IO_3^-/I^-, the anion signal ratios are within one standard deviation of unity. This test verifies that the ICP can efficiently atomize the sample at an applied power of 1.00 kW. Of course, at considerably lower power this interference might become significant.

<u>Polyatomic Ion Formation.</u> Three mixture solutions were analyzed to assess the extent of polyatomic-ion formation. Two 10 μg/mL halogen solutions containing Cl^-, Br^-, I^- and ClO_3^-, BrO_3^- IO_3^- were analyzed to determine the percentage of each halogen that is converted into the oxide during ion extraction into the mass spectrometer. Fluorine was excluded from these mixtures because its oxides will overlap with those of ^{35}Cl. Based on the lack of an anion effect described above, both samples should be completely dissociated within the plasma and the oxide ion ratios will be the same.

In neither case were the halogen-oxide ions detected. Therefore, based on the absolute ion-count rates for the monatomic ions, the percentages of oxide ions are, at most, a few tenths of a percent. These levels are consistent with those determined on this instrument in the positive-ion mode (18).

A mixture of 10 μg/mL NO_3^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} was also examined for oxides, but of N, C, S and P. Although several background peaks from distilled-deionized water have tentatively been assigned as oxide species, this ionic mixture did not measurably increase their magnitudes. In addition, there were no observable increases at any of the masses corresponding to the monatomic ions. The only polyatomic ions that were noted were PO_2^- and PO_3^- at m/z = 63 and 79. The signal intensity for PO_3^- was large enough to suggest a detection limit for P, as PO_4^{3-}, approximately equal to 10 ng/mL. The detection of this ion is not especially surprising because PO_4^{3-} is well know to be a vaporization interferent in ICP-OES; however, whether or not other forms of P can be detected as sensitively by ICP-MS has yet to be determined. It should be noted that the lack of polyatomic ion formation observed here is contradictory to the preliminary observations of others (22).

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TABLE I - ICP operating conditions for both positive and negative-ion detection modes.

Forward Power	1.00 kW
Reflected Power	<10 W
Coolant (Outer) Gas Flow Rate	10.0 L/min
Auxiliary (Intermediate) Gas Flow Rate	0.50 L/min
Nebulizer (Inner) Gas Flow Rate	0.60-0.70 L/min
Sample Uptake Rate	0.50 mL/min
Sampling Height Above The Load Coil	10 mm

.

TABLE II - Comparison of the S/N for selected nonmetal analytes in the positive and negative-ion detection modes.

Element	Isotope	Signal to Background-Noise Ratio[a]	
		Positive Ion	Negative Ion
Boron	11	1160	ND[b]
Fluorine	19	ND	34.5
Silicon	28	95.6	ND
Phosphorus	31	507	ND
Sulfur	34[c]	23.4	ND
Chlorine	35	197	560
Arsenic	75	8090	ND
Selenium	78[c]	239	ND
Bromine	79	843	856
Tellurium	130	2300	ND
Iodine	127	3770	431

a - analyte concentrations are 10 μg/mL.

b - not detectable.

c - isotopes that are not most abundant.

TABLE III - Detection limits for the halogens in the negative-ion mode.

Element	Isotope	Detection Limit[a] (ng/mL)
Fluorine	19	400
Chlorine	35	80
Bromine	79	10
Iodine	127	70

a - S/N = 3, time constant = 1 s.

b - F and Cl would have detection limits of 30 and 20 ng/mL, respectively, in a non-blank-limited situation.

TABLE IV - Effect of the form of the analyte in the sample.

Anion Ratio	Signal Ratio[a]
ClO_3^-/Cl^-	0.986 ± 0.061
ClO_4^-/Cl^-	0.993 ± 0.050
BrO_3^-/Br^-	1.018 ± 0.079
IO_3^-/I^-	1.093 ± 0.055

a - halogen concentrations are 10 μg/mL; each signal ratio and the listed standard deviation are the result of six injections.

FIGURE CAPTIONS

Figure 1.   Negative-ion background spectrum of distilled-deionized

water.   The vertical scale is linear and the 10X insert

has been displaced upwards for clarity.   See text for

peak assignments.

Figure 2.   Response of the halogens as a function of their electron

affinities.   The signals have been corrected for isotope

abundance and instrumental mass bias.   Concentration of

each element is 10 μg/mL.

Figure 3.   Effect of the associated cation on the determination of

10 μg/mL Cl.   Each point is the average of six injections

and the error bars correspond to one standard deviation.

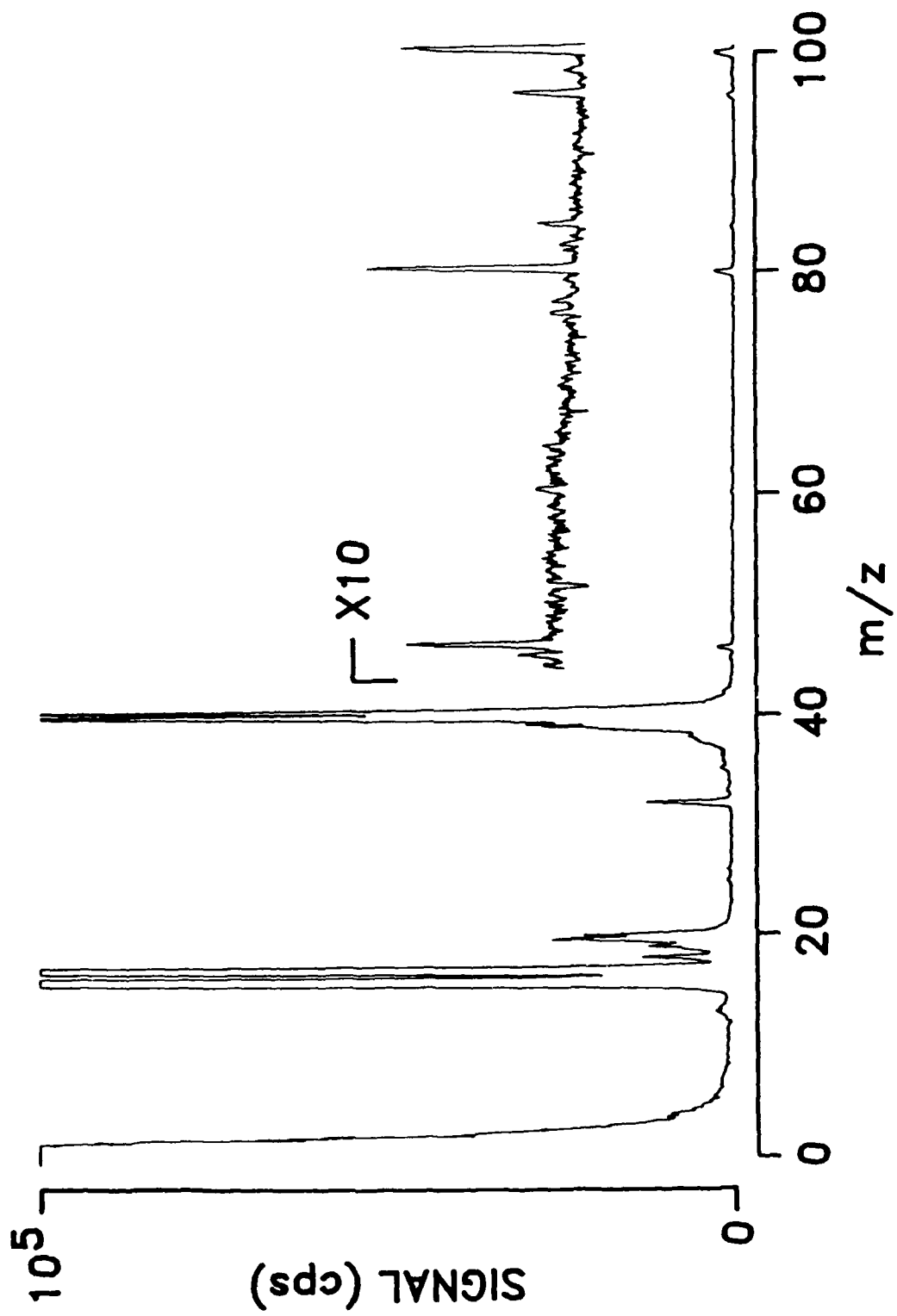The cations have been arranged alphabetically on the
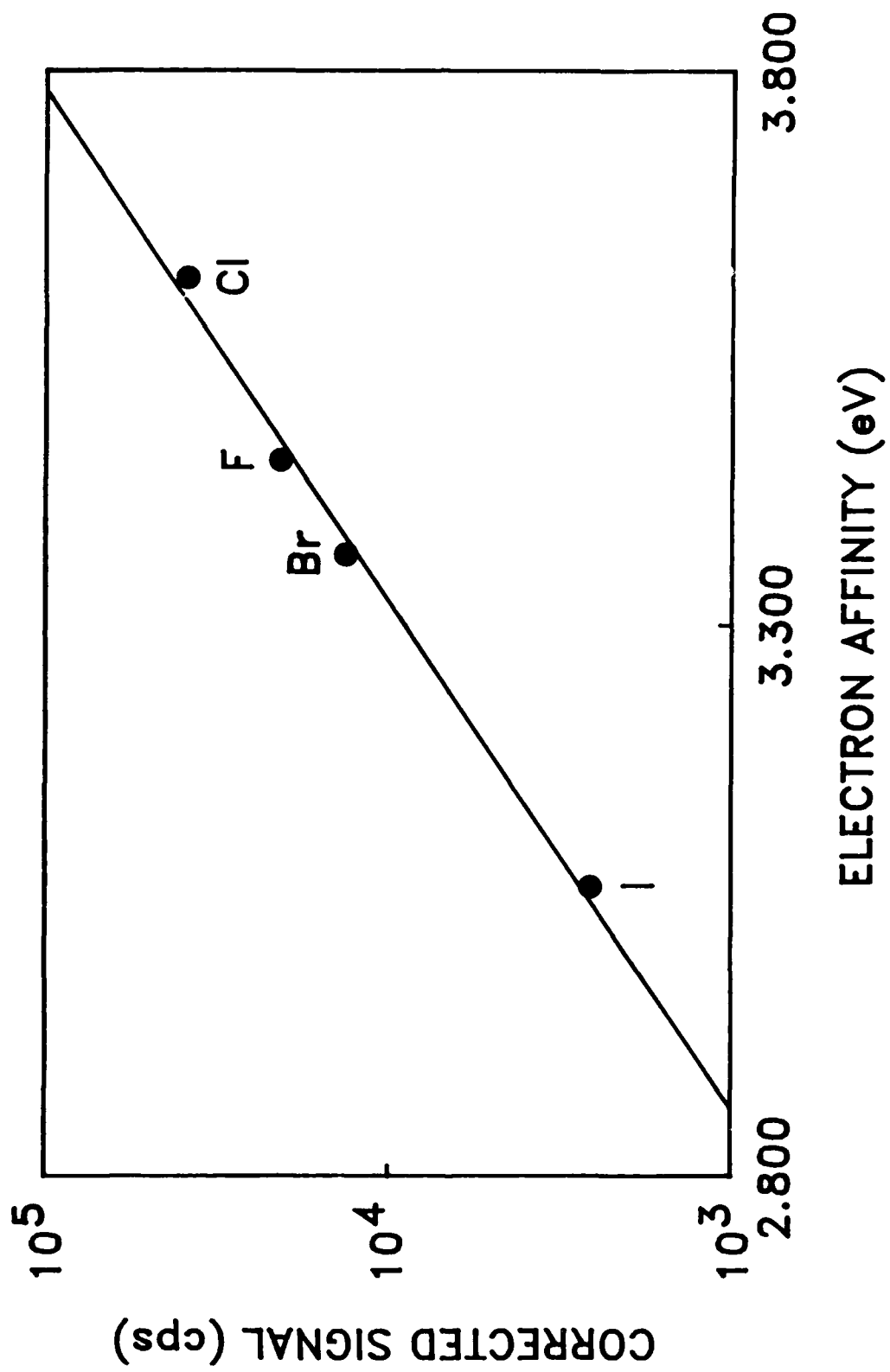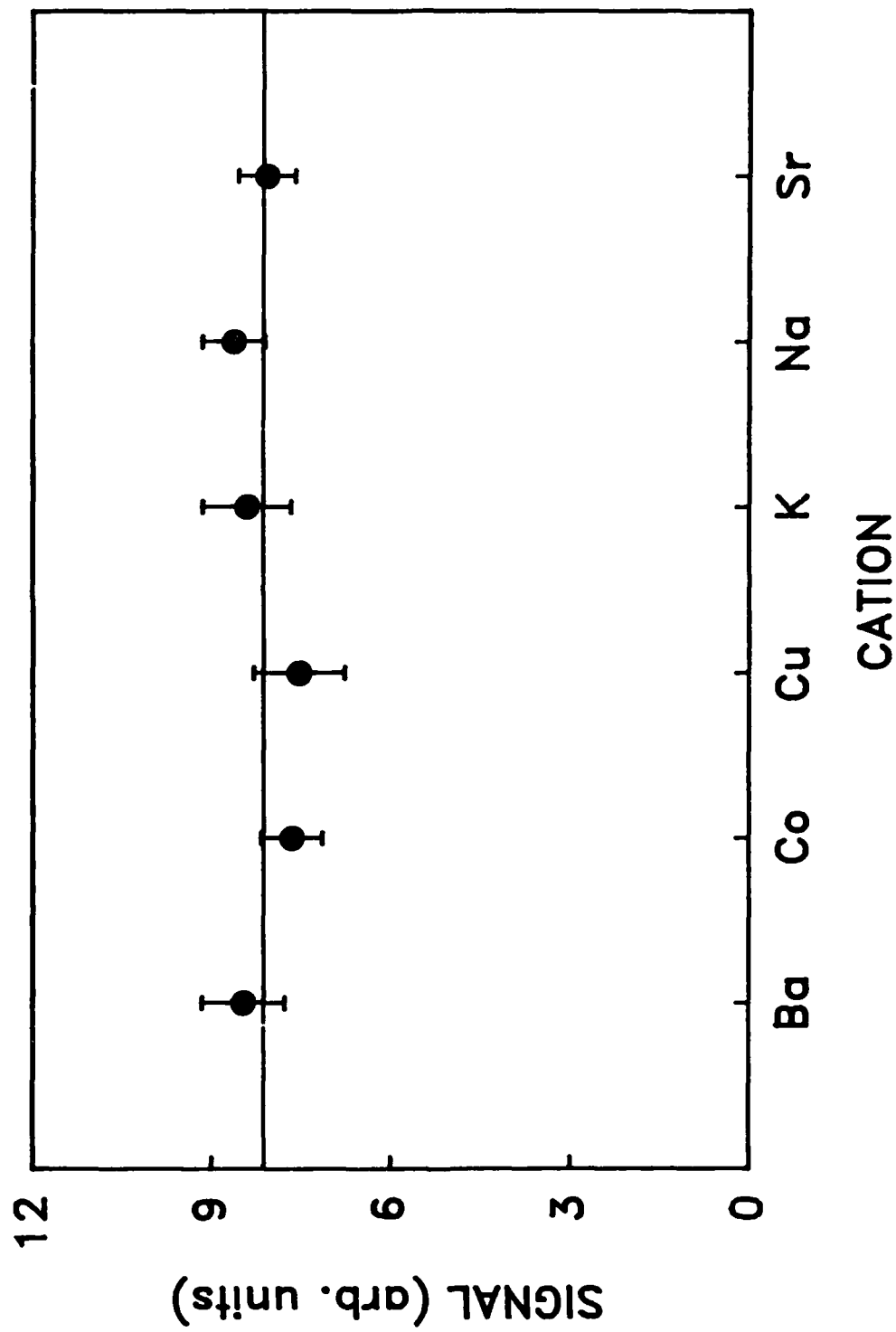
horizontal axis.

Fig. 1

CORRECTED SIGNAL (cps) vs ELECTRON AFFINITY (eV)

Fig 2

SIGNAL (arb. units) vs CATION: Ba, Co, Cu, K, Na, Sr

Fig. 3

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